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AlN matrix composites fabricated by the spark plasma sintering –reactive synthesis method

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A mixture of Al and BN powders was adopted to synthesize AlN matrix composites using the spark plasma sintering-reactive (SPS) synthesis method. The crystalline phases of sintered samples were characterized by X-ray diffraction (XRD). Scanning electron microscope (SEM) and transmission electron microscope (TEM) images of the microstructure revealed that the BN phase was homogeneously distributed in the matrix of synthesized AlN. The effect of sintering temperature on the microstructure and properties of sintered samples was investigated. The results showed that densification of sintered samples was improved and the thermal conductivity exhibited a significant increase with an increase of the sintering temperature.

Key words: SPS, Thermal conductivity, Dielectric property.

Introduction

Hexagonal boron nitride has attracted more attention in recent years, due to its excellent dielectric properties, good thermal shock resistance, and good dielectric property. It will be a potentially promising material to be applied in the engineering and electronic industries. However, its application is limited significantly due to its low strength. It is well known that AlN has a low coefficient of thermal expansion (CET) close to that of silicon, a high thermal conductivity, a low dielectric constant and a high dielectric strength. Therefore, it is expected that AlN-BN composites have a high thermal conductivity, a good dielectric property and good machinabilty [1-2].

AlN-BN composites are generally fabricated by hot-pressed sintering with synthesized AlN and BN powders as starting materials [1-3]. Moreover, commercial AlN is very expensive, and it is inevitable that AlN powders will react with oxygen, which will lead to the decrease of the purity of AlN. Reaction synthesis is a powerful process to obtain better composites with finer and more homogenous microstructures, higher chemical and microstructural stability at high temperature in comparison to those obtained by conventional processes. However, less work has been carried out on the reaction synthesis of AlN matix composites. In this paper, a novel and low cost process route was used to fabricate AlN matrix composites. A mixture of Al and BN powders was used as starting materials, and spark plasma sintering (SPS) was employed to obtain densified composites. The advantage of this route is that the synthesized AlN phase tends to keep clean and active free from gas absorption or oxidation [4-9].

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Experimental Procedure

The method of processing is as shown in Fig. 1. The starting materials were commercial powders of Al (99.8% purity, 6-8 μm), and BN (99.9% purity, 0.5-0.7 μm). Al

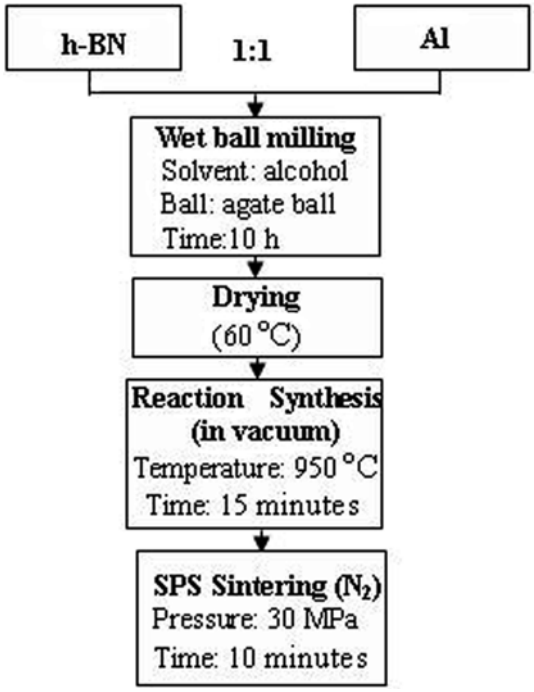

Fig. 1. The process of the preparation of AlN matrix composites.

and BN powders with a molar ratio 1 : 1 were mixed by ball-mixing with alcohol as the grinding media and agate milling balls in polyethylene for 10 h. After drying at 60 °C, the mixture was kept in vacuum at 950 °C for 15 minutes, and then the temperature was raised to the determined temperatures. The reaction products were sintered at different temperatures under a uniaxial pressure of 30 MPa in a nitrogen atmosphere by SPS.

The specimens were ground into 8 mm × 8 mm × 2.5 mm wafers for the measurement of thermal conductivity, and the dielectric constant was measured by a radio frequencies (RF) impedance analyzer (Agilent 4292 A). Water displacement was used to measure the bulk density. X-ray diffraction (XRD, D/MAX-R) was performed to characterize the phases of the products. Scanning electronic microscopy (JSM-5610LV) and transmission electron microscopy (TEM, JEM-2010) were used to evaluate the microstructure of the specimens, and the elements present were determined by energy dispersive X-ray spectroscopy (EDS).

Results and Discussion

Phase compositions

Fig. 2(a) shows the XRD patterns for the mixture of Al and BN heat treated at 950 °C for 15 minutes. Wide and weak peaks of AlN and AlB_2 can be found in Fig. 2(a). Additionally, a portion of peaks of Al are observable as well in Fig. 2(a). Fig. 2(b) presents XRD patterns of samples sintered at different temperature. From Fig. 2(b), it can be seen that only peaks of AlN and BN are observable and the peaks have sharpened. The disappearance of the peaks of Al and AlB_2 indicates that AlN was formed via the appropriate reactions.

Herein, we will explain the reason that the reaction temperature is determined to be 950 °C. According to the literature, when Al reacts with BN under vacuum, there are two possible products and one is AlB_2 and the other is AlB_{12}. AlB_2 will be formed when the reaction temperature is lower than 975 °C. If the temperature is higher than 975 °C, the other product AlB_{12} will be produced [10]. Generally, AlB_2 is not stable at high temperature and is easily nitrided at a certain temperature in nitrogen atmosphere and transformed into AlN and BN, while AlB_{12} has more chemical stability. The reaction formula between AlB_2 and nitrogen can be expressed as : $AlB_2 + 1.5N_2 \rightarrow AlN + 2BN$ [7]. In order to ensure the above available reaction, the reaction temperature was determined to be 950 °C in this study.

Microstructure characterization

Fig. 3 shows SEM micrographs of fracture surfaces of AlN matrix ceramics sintered at different temperatures. These reveal that the grains grow gradually with an increase in the sintering temperature. From Fig. 3(a), there are still some transient phases and grain boundaries are not very obvious, which reveals that the grains have not yet been grown fully. Substantial grain growth is observed

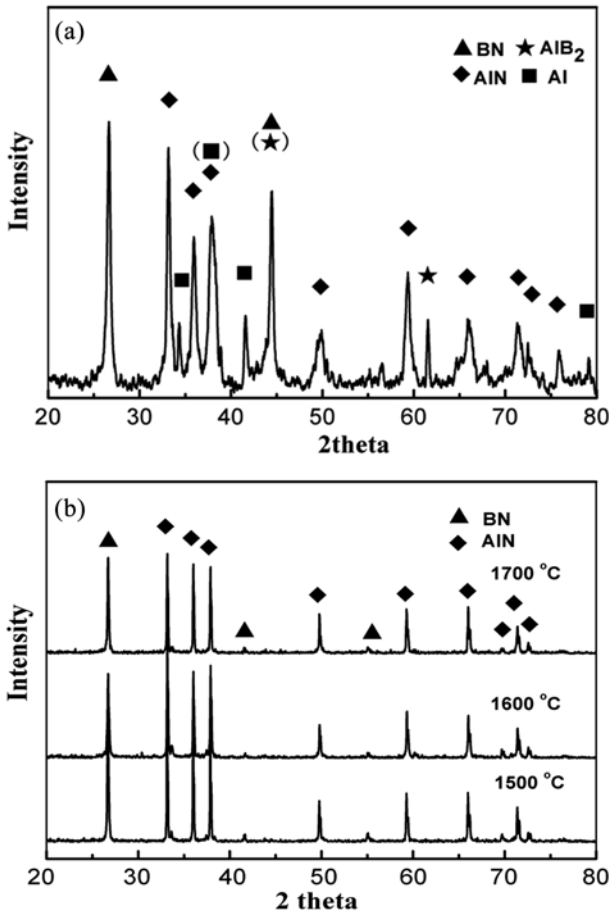

Fig. 2. XRD patterns of samples under different conditions. (a) XRD pattern of the powder synthesized at 950 °C; (b) XRD patterns of the samples sintered at different temperatures.

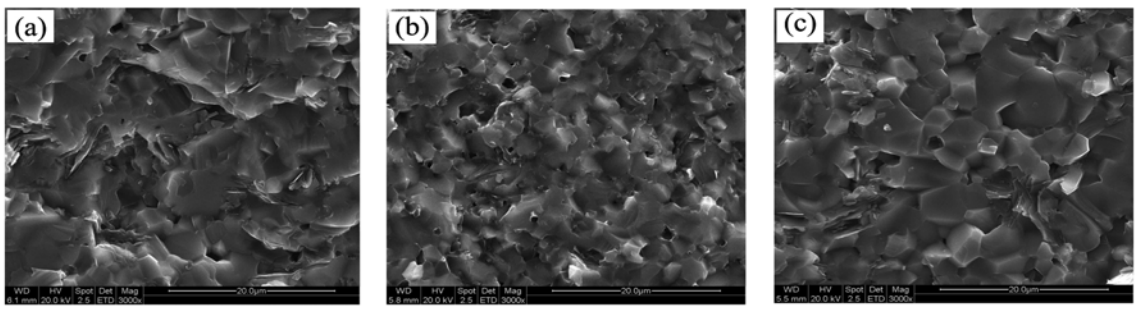

Fig. 3. SEM micrographs of fracture of samples sintered by SPS at different temperatures (a) 1500 °C; (b) 1600 °C; (c) 1700 °C.

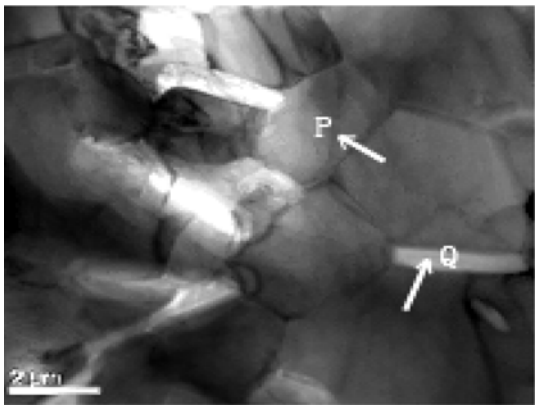

Fig. 4. TEM micrograph for the sample sintered at 1700°C.

with an increase in the sintering temperature and well faceted grains develop upon grain growth, as shown in Fig. 3(c). Fig. 4 shows a transmission electron micrograph (TEM) for the sample sintered at 1700°C. It can be observed that AlN has a polyhedral morphology and the uniform AlN grain size is 3ìm. At the same time, it can also be shown that BN has a flakelike morphology and a secondary BN phase is located at AlN grain boundaries. Fig. 5(a) is the EDS spectrum of point P with elements Au, N and Al. Fig. 5(b) is the EDS spectrum of point Q with elements Au, B, N, and Al. With a combination EDS and XRD, point P can be inferred as AlN phase and point Q as BN phase. The presence of element Au results from the impurities of the preparation of specimens for measurement.

Spark plasma sintering (SPS) is a promising technique that enables ceramic powders to be fully densified at a relatively low temperature in a short time [11-12]. The heating mode is special compared to conventional sintering techniques. The heating is transferred by spark discharge generated by an instantaneous pulsed direct current which is applied through the top and bottom electrode, therefore, such a mode facilitates the heat to reach the surface of the powder in an extremely short time and simultaneously the particle surface is also activated. Therefore densified samples are obtained in a very short time.

Density and thermal conductivity

The variation of thermal conductivity and density of as-sintered samples with respect to sintering temperature is shown in Fig. 6. The real bulk density was used to elevate the densification of as-sintered samples in this paper. It can be shown that the values of density and thermal conductivity increased with an increase in the sintering temperature. This is attributed to the improvement of as-sintered samples densification with a sintering temperature increase. At high temperature, the pores were eliminated and the samples became much denser. From Fig. 6, it is clear that the thermal conductivity of the as-sintered AlN matrix has the same variation tendency as the density.

Dielectric Properties

Fig. 7 shows the relationship between dielectric constant

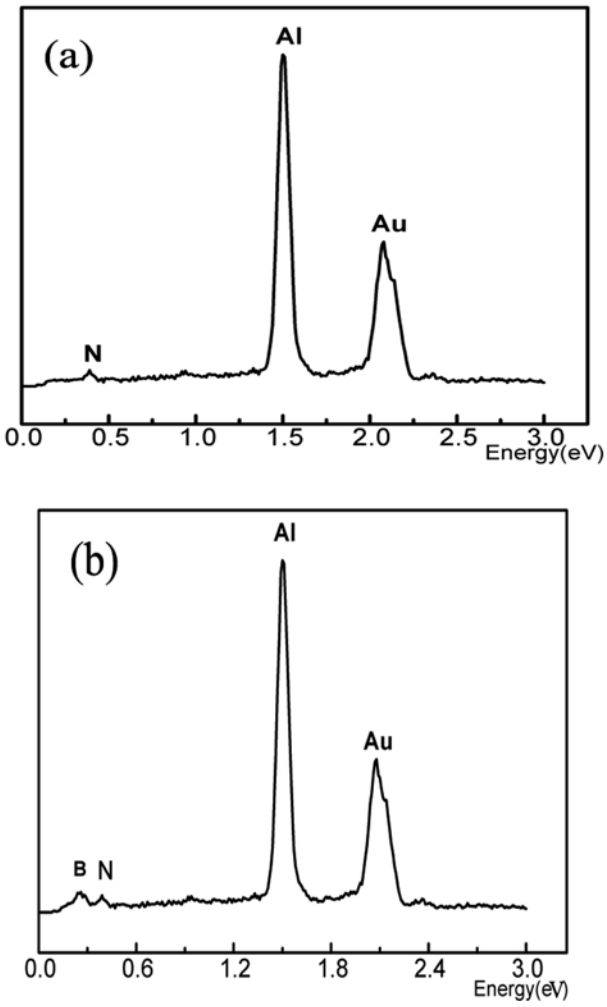

Fig. 5. EDS spectra of the obtained samples (a) point P and (b) point Q.

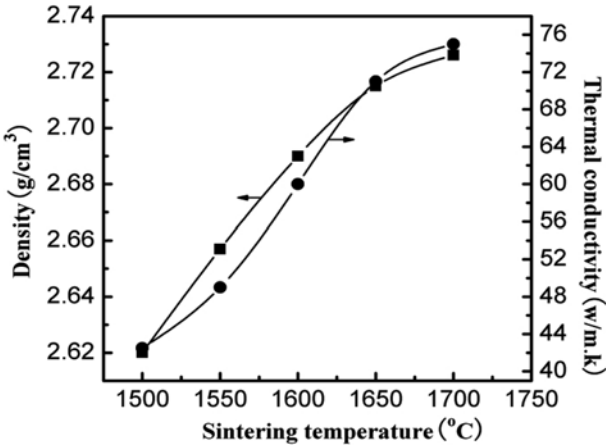

Fig. 6. Variation of hardness and density of as-sintered samples with respect to sintering temperature.

and sintering temperature. It can be seen that the dielectric constant decreases with an increase in the sintering temperature. This result was attributed to the growth of the grains. With the grains growing larger, the content of grain boundary phases decreases, and the binding across

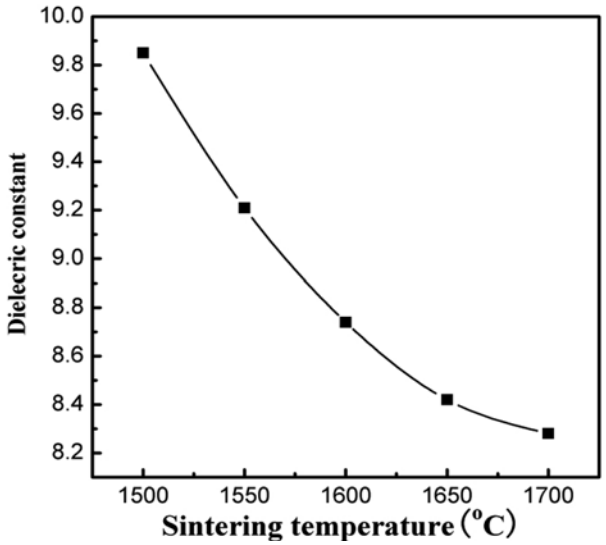

Fig. 7. Variation of dielectric constant with respect to sintering temperature.

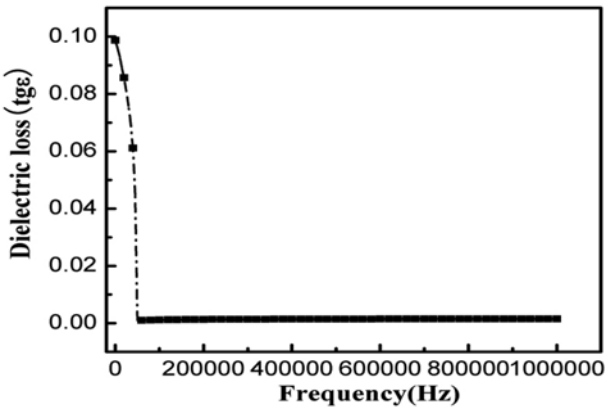

Fig. 8. Variation of dielectric loss with respect to frequency.

boundaries is improved. All the above factors are useful in improving the dielectric constant of AlN-BN [13-14]. Fig. 8 shows dielectric loss dependency on frequency for samples sintered at the temperature of 1700 °C. From this curve, it can be seen that the value of the dielectric loss decreases with an increase in the frequency initially, and then the value tends to remain constant. This result is caused by the difference between the relaxation of the polarization and the variation of the electric field. When the relaxation of the polarization is far behind the variation of the electric field, the values of the dielectric loss fluctuate within a small range. From these results, the conclusion is that the dielectric loss of the samples in these experiments is inferior to that of a single AlN phase bulk ceramic. Dielectric loss would degenerate due to the introduction of crystal imperfections, such as defects, dislocations, pores, microcracks, grain boundaries, second phases and impurities etc. It is confirmed that AlN matrix composites display some of the characteristic of a semiconductor, and the polarization mechanism of the AlN matrix is mainly the space charge polarization. Therefore, AlN matrix composites with a high BN content may have relatively large conduction currents [14-15].

Conclusions

AlN matrix composites were fabricated by the SPS reactive synthesis method at a relatively low temperature. The effect of sintering temperature on the microstructure and properties were investigated in detail. The results show that a sintering temperature increase can promote the densification of as-sintered samples. Larger grains are beneficial to improve the dielectric properties. The value of the dielectric constant decreases slightly with an increase of the sintering temperature. The dielectric loss changed slightly at the initial stage and remained constant at higher frequency. This result is caused by the polarization being far behind the variation of the electric field.

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